

**Program for NECZA 2006**  
**December 8, 2005**  
**University of Pennsylvania, Philadelphia**

Registration, Posters 8:30 – 9:30 am

Victor S.-Y. Lin 9:30-10:10 Gatekeeping effect: multifunctional mesoporous silica nanoparticles for selective catalysis and conversion of bio-based feedstocks to biodiesel, Iowa State University

M. J. Nash 10:10-10:40 Photocatalytic activity of V-substituted ETS-10,  
R. F. Lobo University of Delaware  
A.-M. Zimmernan  
D. Doren

Break 10:40-10:50

K. D. Hammond 10:50-11:20 Physical adsorption on intact zeolite membranes  
G. A. Tompsett and its implications for transport, University of  
S. M. Auerbach Massachusetts Amherst  
W. Curtis Conner, Jr.

D. E. W. Vaughan 11:20-11:50 Influence of T-atom variations on the synthesis of sulfate and selenate sodalites, Pennsylvania State University

Lunch 11:50-1:00

Poster session II 1:00-1:30 pm

D. L. Dorset 1:30-2:10 pm Electron diffraction in zeolite structure determination, a complement to powder diffraction, ExxonMobil

W. F. Hoelderich 2:10-2:50 pm The Use of Renewable Feedstocks as a Contribution for Environmental Protection, University of Technology, RWTH Aachen,

Break 2:50-3:00 pm

Business Meeting 3:00-3:10 pm

Wei Huang 3:10-3:40 pm Selective hydrogenation on zeolite-supported bimetallic catalysts, University of Delaware  
R. F. Lobo  
J. G. Chen

Student Minitalk I 3:40-3:50 pm

Student Minitalk II 4:00-4:10 pm

Student Minitalk III 4:10-4:20 pm

Adjourn 4:20 pm

## Gatekeeping Effect: Multifunctional Mesoporous Silica Nanoparticles for Selective Catalysis and Conversion of Bio-based Feedstocks to Biodiesel

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We have developed a new synthetic strategy for multifunctionalization of mesoporous silica nanoparticle (MSN) materials. This method allows us to tune the relative ratio of different functional groups and the resulting particle morphology of MSNs. By introducing two organoalkoxysilanes as precursors in our co-condensation reaction, we can utilize one precursor with *stronger structure-directing ability* to create the desired pore and particle morphology and employ the *other* for selective immobilization of catalysts. As a proof of principle, we have synthesized and reported a series of bifunctionalized MSN-based heterogeneous catalysts for nitroaldol (Henry) reaction. A common 3-[2-(2-aminoethylamino)ethylamino]propyl (AEP) primary group and three different secondary groups, ureidopropyl (UDP), mercaptopropyl (MP), and allyl (AL) functionalities, were incorporated into these mesoporous silica materials by introducing equal amounts of AEP-trimethoxysilane with UDP-, MP- or AL-trialkoxysilane precursors to the aforementioned co-condensation reaction. The AEP group served as a catalyst and the other secondary groups provided different non-covalent interactions to reactants and thereby controlled the reaction selectivity. By varying the secondary group in these bifunctionalized MSN catalysts, we have discovered that the selectivity of a nitroaldol reaction of two competing benzaldehydes reacting with nitromethane could be systematically tuned simply by varying the physicochemical properties of the pore surface-bound secondary groups, *i.e.* polarity and hydrophobicity.

Furthermore, we have reported a new cooperative catalytic system comprised of a series of bifunctionalized mesoporous silica nanosphere (MSN) materials with various relative concentrations of a general acid, ureidopropyl (UDP) group, and a base, 3-[2-(2-aminoethylamino)ethylamino]propyl (AEP) group. We were inspired by the fact that enzymes engaged in carbonyl chemistry often employ both general acid and base catalytic residues in the active sites to cooperatively activate specific substrates. In this system, we have demonstrated that the general acid group, UDP, could cooperatively activate substrates with the base group, AEP, in catalyzing various reactions that involve carbonyl activation, such as aldol, Henry and cyanosilylation reactions. By further utilizing this approach, we have developed a calcium silicate mixed oxide catalyst that contains both Lewis acidic and basic sites for the synthesis of biodiesel from various free fatty acid (FFA)-containing oil feedstocks. We have demonstrated that the acid and base functionalities could cooperatively catalyze both the esterification of FFAs and the transesterification of oils with short-chain alcohols (e.g. methanol and ethanol) to form alkyl esters (biodiesel). We envision that these multifunctionalized MSNs could serve as new selective catalysts for many other important reactions.

**ELECTRON DIFFRACTION IN ZEOLITE STRUCTURE DETERMINATION, A COMPLEMENT TO POWDER DIFFRACTION.** Douglas L. Dorset, CSR, ExxonMobil Research and Engineering Co., 1545 Route 22 East, Annandale, New Jersey 08801 USA; e-mail: d.l.dorset@exxonmobil.com

Because electron diffraction can sample individual microcrystals, it is clear that this single crystal method can facilitate, in at least two ways, structure determination for inorganic materials, such as zeolites, that are preferentially microcrystalline. First, in a qualitative application, three-dimensional tilts of individual small crystals, to map the reciprocal lattice, greatly simplifies unit cell and space group determination when powder diffraction indexing programs fail. This procedure has been particularly effective in recent structure analyses in our laboratory. It requires, however, a material relatively free from impurities. (On the other hand, this method can also help one to identify impurities.) If incoherent multiple scattering leads to violation of systematic absences, these absences can be restored by collection of precession diffraction patterns based on the Vincent-Midgley method [1], as demonstrated recently [2] - so that the true symmetry is apparent from these patterns. The second, quantitative application, i. e. *ab initio* structure determination from electron diffraction intensity data, often is feasible. In the auspicious case of thin layered zeolite crystals in the MWW framework, the three-dimensional structure was determined by direct methods based on maximum entropy and likelihood [3], the only difficulty arising from the 'missing cone' of structural information imposed by the goniometric tilt limit. Possible methods for restoration of the missing information, although approximately provided by phase and amplitude prediction (Sayre equation), include alternate crystallization of the desired crystal projection by appropriate structure directing agents, or, simply, by sectioning the desired view of the structure in available samples. Multiple scattering perturbations include both n-beam dynamical and secondary scattering; collection of precession data greatly reduces the latter influence [2], improves the prospect of *ab initio* analyses *via* direct methods (e. g. tests on LTA, ITQ-1, ITQ-7, ZSM-10, MOR, MCM-68), although systematic dynamical diffraction is still observed (even at 300 kV). Improved collection of intensity data *via* imaging plates, exploiting a much greater linear response to intensity, is also recommended. Generally, for unknown zeolite structures, electron diffraction analyses have been carried out in parallel with the usual powder determinations, not only to provide needed symmetry information but also to detect structural details of important zones, e. g. the location of porous channels to guide the powder determination; in some cases, the crystal structure would not have been solved easily without this electron crystallographic information.

[1] Vincent, R.; Midgley, P., *Ultramicroscopy* 1994 **53**, 271.

[2] Dorset, D. L.; Gilmore, C. J.; Jorda, J. L; Nicolopoulos, S., *Ultramicroscopy*, in press.

[3] Dorset, D. L.; Roth, W. J.; Gilmore, C. J., *Acta Cryst.* 2005 A61, 516.

## Influence of T-atom variations on the synthesis of sulfate and selenate sodalites.

David E. W. Vaughan

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The **SOD** structure is one of the most versatile in that it tolerates major T-atom variations (Si, Al, Ga, Ge, Zn, P, Be, Fe, etc) and can occlude numerous different anionic and molecular species. Various blue, green and red sodalites are used as pigments, and in the case of the blue “lapis lazuli”, in jewelry. Other forms have been extensively studied for hydrogen storage; trapping nuclear waste products such as  $^{85}\text{Kr}$  and semiconductor nano-clusters; and the properties of photochromism and cathodochromism. Much of the latter work targeted applications in information storage and in military radar display phosphors. The main interest in this paper is to establish the influence of changing T-atoms in a novel blue-**SOD** made with trapped  $\text{TMA}^+$  and  $\text{SO}_4^{2-}$ , in which the reductants formed during the tetramethyl ammonium burn-off reduces the sulfate to  $\text{S}_2$  (yellow) and  $\text{S}_3$  (blue) clusters. Whereas the sulfur clusters induce green and blue colors, selenium clusters induce a red coloration.

Keeping the basic formulation constant at;

0.9  $\text{TMA}_2\text{O}$ ; 1.45  $\text{Na}_2\text{O}$ ;  $\text{Al}_2\text{O}_3$ : 3  $\text{SiO}_2$ : 120  $\text{H}_2\text{O}$ ;  $\text{Na}_2(\text{SO}_4, \text{SeO}_4)$

and replacing Al and Si with Ga and Ge to give the additional combinations Ga/Si, Ge/Si, Al/Ge and Al/Ga with either sulfate or selenate. Experiments were conducted at 100°C, 150°C and 180°C in 23ml or 45ml Parr Teflon<sup>®</sup> lined acid digestion bombs.

Crystalline products were produced in all the silica containing reactions. In the non-silica selenate reactions (Ga/Al; Ga/Ge) clear solutions were obtained at 100°C and 150°C, and a dark- red brown solution resulted at 180°C comprising a suspension of nano-crystalline selenium metal. Sodalites are the predominant products for most of the substitutions. In the base case (Si/Al/ $\text{SO}_4$ ) **FAU** is replaced by **SOD** then **ANA** with increasing temperatures and reaction times. Replacement of sulfate with selenate results in the displacement of **SOD**, first by **LTA** then **CAN**. Substitution of Al by Ga replicates the base case for both anions. When Ge replaces Si results are similar, except that **SOD** and **CAN** co-crystallize over the full temperature range for both anions. In the Ga/Ge compositions, large crystals of **SOD** (>100 $\mu$ ) are common. **SOD** is the dominant phase at 100°C, but is replaced by a microcrystalline Na,H-gallosilicate (a polymorph of  $\text{Na}_3\text{HGe}_7\text{O}_{16}(\text{H}_2\text{O})_4$ ; ICDD file 01-076-0102) at higher temperatures. Only the Si/Al/ $\text{SO}_4$  calcined **SOD** materials produced colored products.

Related studies:

D. Arieli, D.E.W. Vaughan and D. Goldfarb, “New synthesis and insight into the structure of blue ultramarine pigments”, *J. Amer. Chem. Soc.*, 126, 5776 (2004).

D.E.W. Vaughan, H.P. Yennawar and A.J. Perrotta, “Synthesis and structure of large optically clear crystals of Ga/Ge-sodalite”, *Cryst. Growth&Design*, 6, 2072 (2006).

# Physical Adsorption on Intact Zeolite Membranes and Its Implications for Transport

Karl D. Hammond      Geoffrey A. Tompsett  
Scott M. Auerbach      W. Curtis Conner, Jr.

November 10, 2006

## Abstract

Physical adsorption has been used for decades to analyze and predict the properties of porous materials such as zeolites. Adsorption measurements are also important to interpreting zeolite membrane permeation, as the adsorption isotherm gives an indication of the concentration dependence of the diffusion coefficient in the zeolite. However, the properties of zeolite membranes may or may not be equivalent to those of zeolite powders, and the influence of the support (which is a significant fraction of the overall mass) is still not clear and likely depends on the type of support used.

We have developed a method to measure adsorption on membranes without changing the membranes in the process. We disentangle the contributions from the support from those of the zeolite, and use the resulting adsorption isotherms to determine the ratio of the Fick diffusivity to the Maxwell-Stefan diffusivity. These factors are used as input to a calculation of the flux through a supported membrane using a constant Maxwell-Stefan diffusion coefficient in the zeolite and support.

The flux through the membrane is compared to that using a powder, supported (hypothetically) on the same variety of support. In this fashion, we get an estimate of the relative importance of the support, and determine the effects of any multiscala porosity in the membrane on the flux. The results indicate no detectable mesoporosity in the membrane and no significant differences between powder and membrane permeation for these membranes. The results also indicate that the support strongly influences the overall permeance for most relative magnitudes of the diffusion coefficient. It is important, however, to note that other membranes grown by other methods may have detectable mesoporosity, and that these mesopores may exert a strong influence on transport.

## Photocatalytic activity of Vanadium-substituted ETS-10

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## SUMMARY

Incremental amounts of V have been isomorphously substituted for Ti, along with the complete substitution of V for Ti to form the analogous structure AM-6. Results show a reduction of the band gap energy along with increased photocatalytic activity with respect to ETS-10. NEXAFS and Raman spectroscopy have been used to confirm the presence of two different oxidation states for vanadium, along with considerable disorder along the chains, which is believed to explain the trends in the band gap energy. All these experimental results have been closely tied to small cluster ONIOM models by Zimmerman et. al.<sup>1</sup>

# Selective Hydrogenation on Zeolite-Supported Bimetallic Catalysts

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## Abstract

Novel catalysts have been developed by supporting Pd-based bimetallic nanocatalysts on zeolites to achieve higher selectivity for the selective hydrogenation of acetylene in a stream containing excess ethylene at relatively low temperatures (300-339K). Low-temperature hydrogenation offers the opportunity of using competitive adsorption to achieve preferential hydrogenation of acetylene. Previous work from our group has found that bimetallic catalysts favor low temperature hydrogenation.<sup>[1-3]</sup> Results from many other groups have also shown that Pd is a good catalyst for the selective hydrogenation of alkynes in excess ethylene. Therefore the strategy of the present work was to modify Pd catalysts and to embed bimetallic nanoparticles in an environment that is highly selective for acetylene hydrogenation.

Cation- $\pi$  interaction offers the potential for selective adsorption of acetylene on the zeolite supports. In the current work we used the ion-exchanged  $\beta$ -type zeolite<sup>[4, 5]</sup> as the support of the bimetallic catalysts. The zeolite structure should have multiple dimensions and contain large pores, in order to house the bimetallic nanoparticles inside the pores.

Flow reactor studies using GC, batch reactor studies using FTIR, EXAFS and CO-Chemisorption evaluation have been performed. Our results indicate that the Pd-Ag bimetallic catalyst has a much higher selectivity for acetylene hydrogenation in excess ethylene than either Pd or Ag. Modeling of reactions in FTIR shows significant differences in the hydrogenation rate constant, adsorption equilibrium constant, as well as the selectivity of the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> supported catalysts and  $\beta$ -zeolites supported catalysts, with  $\beta$ -zeolite supported catalysts showing much higher selectivity than the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> supported catalysts.

[1] H.H. Hwu, Joseph Eng, Jr., J.G. Chen, *JACS*, 124(2002), 702-709

[2] N.A. Khan, H.H. Hwu, J.G. Chen, *J. of Catal.*, 205(2002) 259-265

[3] J.R. Kitchin, J.K. Nørskov, M.A. Barteau J.G. Chen, *Phy. Rev. Letter*, 93(2004) 156801

[4] Martinez-Inesta, M. M.; Peral, I.; Proffen, T.; Lobo, R. F., *Studies in Surface Science and Catalysis (2004), 154B(Recent Advances in the Science and Technology of Zeolites and Related Materials)*, 1393-1399

[5] Feuerstein, M.; Lobo, R. F., *Chemistry of Materials (1998), 10(8), 2197-2204*